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PATENT ABSTRACTS OF JAPAN

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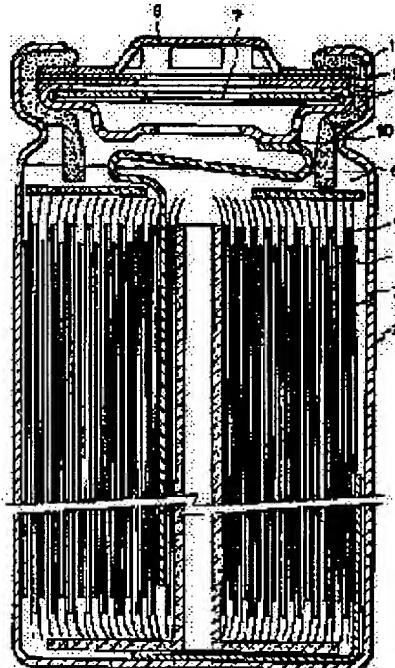
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(54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a large capacity secondary battery which has large capacity and excellent charge and discharge characteristics by containing triester phosphate in nonaqueous electrolyte in a nonaqueous electrolyte secondary battery.

SOLUTION: In a nonaqueous electrolyte secondary battery composed of a positive electrode 5 which contains material capable of reversibly storing and discharging lithium, a negative electrode 4 which contains three kinds or more of atoms selected from 1, 2, 13, 14, 15 group atoms of a periodic table and is mainly made of an amorphous chalcogen compound and/or an amorphous oxide, nonaqueous electrolyte 6 which contains lithium salt, and a separator 3, at least one kind of triester phosphate is contained in nonaqueous electrolyte.



LEGAL STATUS

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CLAIMS

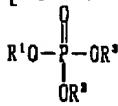
[Claim(s)]

[Claim 1] The nonaqueous electrolyte rechargeable battery characterized by containing at least one sort of trialkyl phosphate in this nonaqueous electrolyte in the negative electrode which mainly consists of an amorphous chalcogen compound and/or an amorphous oxide, the nonaqueous electrolyte containing lithium salt, and the nonaqueous electrolyte rechargeable battery which consists of a separator containing three or more sorts of atoms chosen from the positive electrode containing the material in which occlusion discharge is possible in reversible, periodic tables 1, 2, 13, and 14, and 15 group atom in a lithium.

[Claim 2] The nonaqueous electrolyte rechargeable battery according to claim 1 characterized by showing at least one sort of trialkyl phosphate contained in this nonaqueous electrolyte by the following general formula (1), (2), and (3).

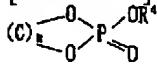
General formula (1)

[Formula 1]



(Among a formula, even if R1, R2, and R3 are the same, they may differ from each other, and they express the phenyl group which is not replaced [the alkyl group which is not replaced / substitution or / substitution, or].) General formula (2)

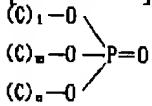
[Formula 2]



(R4 expresses among a formula the phenyl group which is not replaced [the alkyl group which is not replaced / substitution or /, substitution, or].) - (C)- is the hydrocarbon of the shape of a straight chain, and the letter of branching, and k expresses the integer of 2-8.

General formula (3)

[Formula 3]



(-(C)- is the hydrocarbon of the shape of a straight chain, and the letter of branching, and l, m, and n express the integer of 0-12.)

[Claim 3] The nonaqueous electrolyte rechargeable battery according to claim 1 to 2 with which the content of the trialkyl phosphate contained in this nonaqueous electrolyte at least one sort is characterized by being 10 % of the weight from 0.001 % of the weight to the lithium salt contained in the electrolytic solution.

[Claim 4] lithium salt according to claim 3 -- at least -- LiBF4 And/or, LiPF6 it is -- nonaqueous electrolyte rechargeable battery characterized by things

[Claim 5] A nonaqueous electrolyte rechargeable battery given in any 1 term of the claims 1-4 to which a kind is characterized by the thing of this negative-electrode material shown by the general formula (4) at least.

M1 M2pM4qM6r General formula (4)

It Pb(s). the inside of a formula, M1, and M2 -- difference -- Si, germanium, and Sn -- it is chosen out of P, B, aluminum, and Sb -- at least -- a kind and M4 it is chosen out of Li, Na, K, Rb, Cs, Mg, calcium, Sr, and Ba -- a kind

and M6 [at least] are chosen from O, S, and Te -- as for a kind, and p and q, each 0.001-10r at least expresses the number of 1.00-50

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] the thing about the high capacity nonaqueous electrolyte rechargeable battery this invention excelled [rechargeable battery] in the charge-and-discharge cycle property -- it is -- negative-electrode material -- mainly -- an amorphous chalcogen compound -- and -- or it is related with improvement of charge-and-discharge properties, such as a charge-and-discharge cycle life of the big nonaqueous electrolyte rechargeable battery of the service capacity which is an amorphous oxide

[0002]

[Description of the Prior Art] Since it was the high activity which the so-called dendrite by which the lithium metal grew up to be arborescence generates, and the cause of internal short-circuit or the dendrite itself has in charge and discharge as a negative-electrode material for nonaqueous electrolyte rechargeable batteries when they are used although a lithium metal and a lithium alloy are typical, risk, such as ignition, had been entailed. On the other hand, nature material of a baked carbon in which insertion and discharge are possible in reversible has come to be put in practical use in a lithium. Since itself has conductivity, a lithium metal may deposit on carbonaceous material in the case of a surcharge or boosting charge, and the fault of this carbonaceous material makes a dendrite deposit after all. Although a battery charger is devised or the method of lessening a positive active material and preventing a surcharge is adopted in order to avoid this, since the amount per active material is limited therefore, service capacity will also be limited by the latter method. Moreover, since carbonaceous material has comparatively small density, service capacity will be restricted in the double meaning that the capacity per volume is low. sticking by pressure or carrying out a laminating, and using a lithium foil for a carbon material -- JP,61-54165,A and JP,2-82447,A -- said -- 2-215062 -- said -- 3-122974 -- said -- 3-272571 -- said -- 5-144471 -- said -- 5-144472 -- said -- 5-144473 -- said -- although indicated by 5-151995, it was not what is using the carbon material as a negative-electrode active material, and essentially solves the above-mentioned problem

[0003] On the other hand, it is negative-electrode material other than a lithium metal, a lithium alloy, and carbonaceous material. TiS₂ which can do occlusion and discharge of a lithium ion, LiTiS₂ (U.S. patent 983476th), WO₂, and Fe 2O₃ A lithium compound (JP,3-112070,A), Nb 2O₅ (JP,62-59412,B, JP,2-82447,A), an iron oxide, FeO and Fe 2O₃, Fe 3O₄, cobalt oxide, CoO and Co 2O₃, and Co 3O₄ (JP,3-291862,A) are known. The nonaqueous electrolyte rechargeable battery with the high discharge potential which each of these compounds has low oxidation reduction potential, and is 3V class is not realizable. Moreover, what also satisfies service capacity is not made.

[0004] As what attains the nonaqueous electrolyte rechargeable battery in which average discharge voltage has a 3-3.6V class high discharge potential in order to improve the above-mentioned fault, using oxides, such as Sn, V, Si, B, and Zr, and those multiple oxides for negative-electrode material is proposed (JP,5-174818,A, this 6- 60867, this 6-275267, this 6- 325765, this 6- 338324, EP- 615296). Although average discharge voltage of service capacity is large at 3-3.6V class, and oxides, such as these [Sn, V, Si, B, and Zr], and those multiple oxides do not almost have dendrite generating in a practical use field and gave the nonaqueous electrolyte rechargeable battery with very high safety by combining with the positive electrode of the transition-metals compound containing a certain kind of lithium, they had the problem that a charge-and-discharge cycle property was not enough.

[0005]

[Problem(s) to be Solved by the Invention] The technical problem of this invention is raising the charge-and-discharge cycle property of the big nonaqueous electrolyte rechargeable battery of service capacity.

[0006]

[Means for Solving the Problem] The technical problem of this invention was attained by the nonaqueous electrolyte

rechargeable battery characterized by this electrolytic solution containing at least one sort of trialkyl phosphate in the positive electrode which contains the material in which occlusion discharge is possible in reversible for a lithium and a negative electrode, the nonaqueous electrolyte containing lithium salt, and the nonaqueous electrolyte rechargeable battery that consists of a separator.

[0007]

[Embodiments of the Invention] Although the desirable form of this invention is listed below, this invention is not limited to these.

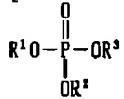
(1) The nonaqueous electrolyte rechargeable battery characterized by containing at least one sort of trialkyl phosphate in this nonaqueous electrolyte in the negative electrode which mainly consists of an amorphous chalcogen compound and/or an amorphous oxide, the nonaqueous electrolyte containing lithium salt, and the nonaqueous electrolyte rechargeable battery which consists of a separator containing three or more sorts of atoms chosen from the positive electrode containing the material in which occlusion discharge is possible in reversible, periodic tables 1, 2, 13, and 14, and 15 group atom in a lithium.

(A nonaqueous electrolyte rechargeable battery given in the term 1 characterized by showing at least one sort of trialkyl phosphate contained in 2 this nonaqueous electrolyte by the following general formula (1), (2), and (3).)

General formula (1)

[0008]

[Formula 4]

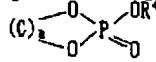


[0009] (Among a formula, even if R1, R2, and R3 are the same, they may differ from each other, and they express the phenyl group which is not replaced [the alkyl group which is not replaced / substitution or / substitution, or].)

General formula (2)

[0010]

[Formula 5]

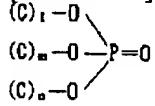


[0011] (R4 expresses among a formula the phenyl group which is not replaced [the alkyl group which is not replaced / substitution or /, substitution, or].) - (C)- is the hydrocarbon of the shape of a straight chain, and the letter of branching, and k expresses the integer of 2-8.

General formula (3)

[0012]

[Formula 6]



[0013] (-(C)- is the hydrocarbon of the shape of a straight chain, and the letter of branching, and l, m, and n express the integer of 0-12.)

(3) A nonaqueous electrolyte rechargeable battery given in either of the terms 1-2 to which the content of the trialkyl phosphate contained in this nonaqueous electrolyte at least one sort is characterized by being 10 % of the weight from 0.001 % of the weight to the supporting electrolyte contained in the electrolytic solution.

(4) a supporting electrolyte given in 3 -- at least -- LiBF4 And/or, LiPF6 it is -- nonaqueous electrolyte rechargeable battery characterized by things

(5) A nonaqueous electrolyte rechargeable battery given in any 1 term of the terms 1-4 to which a kind is characterized by the thing of this negative-electrode material shown by the general formula (4) at least.

M1 M2pM4qM6r General formula (4)

It Pb(s). the inside of a formula, M1, and M2 -- difference -- Si, germanium, and Sn -- It is to be chosen out of P, B, aluminum, and Sb a kind and M4 that it is few. That it is few as being chosen out of Li, Na, K, Rb, Cs, Mg, calcium, Sr, and Ba A kind, M6 It is to be chosen out of O, S, and Te a kind, and p and q that it is few. They are 0.001-10r respectively. The number of 1.00-50 is expressed.

(6) A nonaqueous electrolyte rechargeable battery given in the term 5 to which a kind is characterized by the thing of

this negative-electrode material shown by the general formula (5) at least.

SnM3pM5qM7r General formula (5)

(M3 is chosen from Si, germanium, Pb, P, B, and aluminum among a formula -- a kind and M5 [at least] are chosen from Li, Na, K, Rb, Cs, Mg, calcium, Sr, and Ba -- a kind and M7 [at least] are chosen from O and S -- as for a kind, p, and q, each 0.001-10r at least expresses the number of 1.00-50)

At least one sort of this positive-electrode material (7) Lix CoO₂ and Lix NiO₂, Lix MnO₂, Lix Coa nickel (1-a) O₂, and LixCob V(1-b) Oz, LixCob Fe (1-b) O₂ and Lix Mn 2O₄, Lix Mnc Co (2-c) O₄ and Lix Mnc nickel (2-c) O₄, Lix Mnc V (2-c) O₄ and Lix Mnc Fe (2-c) O₄ (among a formula) x=0.0 2-1.2, a= 0.1 to 0.9, b= 0.8 to 0.98, c=1.6-1.96, a nonaqueous electrolyte rechargeable battery given in the terms 1-6 characterized by ***** which is z= 2.01 to 2.3.

[0014] A charge-and-discharge cycle property can be raised without spoiling the high capacity of a nonaqueous electrolyte rechargeable battery by making the electrolytic solution contain at least one sort of trialkyl phosphate. Although the example of the trialkyl phosphate of this invention is shown below, this invention is not limited to these. As trialkyl phosphate G. M. Kosolapoff and L. Maier, ed., "Organic Phosphorus Compounds", vol. 1-7, and Wiley-Interscience(1972)-(1976). Or edited by Society of Synthetic Organic Chemistry, Japan, an "organic phosphorous compound", Hakuhodo publication (1971), Chemistry of an R&D report No5" organic phosphorous compound, and trialkyl phosphate industrial" and given in CMC issue (1977). (for example, as what is expressed with a general formula (1)) Trimethyl phosphate, phosphoric-acid triethyl, phosphoric-acid TORIPUROPIRU, tributyl phosphate, Trioctyl phosphate phosphoric-acid tris chloro ethyl, phosphoric-acid TORIBUTOKISHI ethyl, A triphenyl phosphate, tricresyl phosphate, cresyl phenyl phosphate, As what is expressed with a general formula (2), Octyl diphenyl phosphate or tricyclohexyl phosphate : Methyl-ethylene phosphate, Methyl trimethylene phosphate, ethyl ECHIEN phosphate, Propyl ethylene phosphate, phenylethylene phosphate, phenyl trimethylene phosphate, Trimethylolethane phosphate etc. can be mentioned as what is expressed with a general formula (3).

[0015] The content of the trialkyl phosphate contained in the electrolytic solution has desirable 1. from 0.0001 in 0.1 mols /to an electrolytic-solution solvent, and its 1. is still more desirable in 0.1 mols /from 0.001 As a content of the trialkyl phosphate to the supporting electrolyte contained in the electrolytic solution, 10 % of the weight is desirable from 0.001 % of the weight, and 0.01 - 5 % of the weight is desirable.

[0016] Generally the electrolytic solution consists of supporting electrolytes dissolved in a solvent and its solvent, and its lithium salt (an anion and lithium cation) is desirable. As a solvent of the electrolytic solution which can be used by this invention, propylene carbonate, Ethylene carbonate, butylene carbonate, dimethyl carbonate, Diethyl carbonate, methylethyl carbonate, gamma-butyrolactone, Methyl formate, methyl acetate, 1, 2-dimethoxyethane, a tetrahydrofuran, 2-methyl tetrahydrofuran, dimethyl sulfoxide, 1, 3-dioxolane, A formamide, a dimethylformamide, a dioxolane, a dioxane, An acetonitrile, a nitromethane, an ethyl monochrome glyme, trialkyl phosphate, Trimethoxy methane, a dioxolane derivative, a sulfolane, 3-methyl-2-oxazolidinone, Non-proton nature organic solvents, such as propylene carbonate derivative, tetrahydrofuran derivative, ethyl ether, 1, and 3-propane ape ton, can be mentioned, and these kinds or two sorts or more are mixed and used. The solvent of a carbonate system is desirable and that in which annular carbonate and/or un-annular carbonate were included is desirable in inside. as annular carbonate -- ethylene carbonate and propylene carbonate -- ** -- it is desirable Moreover, as for un-annular carbonate and the bottom, it is desirable to include diethyl carbonate, dimethyl carbonate, and methylethyl carbonate. As lithium salt dissolved in these solvents that can be used by this invention For example, LiClO₄, LiBF₄, LiPF₆, and LiCF₃ SO₃, LiCF₃ CO₂, LiAsF₆, LiSbF₆, LiB10Cl10, a low-grade aliphatic carboxylic-acid lithium, Li salts, such as LiAlCl₄, LiCl, LiBr, LiI, a chlоро borane lithium, and 4 phenyl lithium borate, can be raised, and these kinds or two sorts or more can be mixed and used. It is LiBF₄ especially. And/or LiPF₆ What was dissolved is desirable. Although especially the concentration of a supporting electrolyte is not limited, its 0.2-3 mols per 1l. of electrolytic solutions are desirable. As the electrolytic solution which can be used by this invention, they are LiCF₃ SO₃, LiClO₄, and LiBF₄ to the electrolytic solution which mixed suitably ethylene carbonate, propylene carbonate, 1, 2-dimethoxyethane, dimethyl carbonate, or diethyl carbonate. And/or LiPF₆ The included electrolytic solution is desirable. They are LiCF₃ SO₃, LiClO₄, and LiBF₄ especially to a mixed solvent with propylene carbonate or ethylene carbonate, 1 and 2-dimethoxyethane and/ or diethyl carbonate. And/or LiPF₆ The included electrolytic solution is desirable and it is ethylene carbonate and LiPF₆ especially at least. What is included is desirable. although especially the amount that adds these electrolytic solutions in a cell is not limited -- a positive active material, the amount of negative-electrode material, and the size of a cell -- **** for initial complements -- things are made

[0017] Hereafter, the other materials and the manufacture method for making the nonaqueous electrolyte rechargeable battery of this invention are explained in full detail. positive and the negative electrode used for the nonaqueous electrolyte rechargeable battery of this invention -- a positive electrode -- a mixture or a negative electrode -- a mixture

can be painted on a charge collector and can be made a positive electrode or a negative electrode -- everything but a positive active material or negative-electrode material can be looked like [a mixture], respectively, and can contain an electric conduction agent, a binder, a dispersant, a filler, an ion electric conduction agent, a pressure reinforcement agent, and various additives in it, respectively

[0018] As for the negative-electrode material used by this invention, it is desirable that it is mainly amorphous at the time of cell inclusion. It is the object which has the broadcloth dispersion band which mainly has the peak from 20 degrees to 40 degrees with 2theta value with the X-ray diffraction method [be / amorphous] using CuK alpha rays said here, and you may have a crystalline diffraction line. the strongest intensity is 500 or less times of the diffraction line intensity of the peak of the broadcloth dispersion band looked at by 20 degrees or more 40 degrees or less with 2theta value among the crystalline diffraction lines preferably looked at by 40 degrees or more 70 degrees or less with 2theta value -- desirable -- further -- desirable -- 100 or less times -- it is -- especially -- desirable -- 5 or less times -- it is -- most -- desirable -- It is not having a crystalline diffraction line.

[0019] As for the negative-electrode material used by this invention, being expressed with the following general formula (4) is desirable.

M1 M2pM4qM6r General formula (4)

The inside of a formula, M1, and M2 It is it a kind that it is few as being chosen out of Si, germanium, Sn, Pb, P, B, aluminum, and Sb in difference, and is Si, germanium, Sn, P, B, and aluminum preferably, and they are Si, Sn, P, B, and aluminum especially preferably. M4 It is it a kind that it is few as being chosen out of Li, Na, K, Rb, Cs, Mg, calcium, Sr, and Ba, and is K, Cs, Mg, and calcium preferably, and they are Cs and Mg especially preferably. M6 It is it a kind that it is few as being chosen out of O, S, and Te, is O and S preferably, and is O especially preferably. p q It is 0.001-10 respectively, is 0.01-5 preferably, and is 0.01-2 especially preferably. r is 1.00-50, is 1.00-26 preferably, and is 1.02-6 especially preferably. M1 and M2 Even if especially a valence is not limited and is an independent valence, it may be the mixture of each valence. Moreover, M1, M2, and M4 A ratio is M2. And M4 M1 It can receive, can be made to change continuously in the range of the 0.001-10-mol equivalent, responds to it, and is M6. An amount (it sets to a general formula (4) and is the value of r) also changes continuously.

[0020] Also in the compound mentioned above, it sets to this invention, and is M1. The case where it is Sn is desirable and is expressed with a general formula (5).

SnM3pM5qM7r General formula (5)

The inside of a formula, and M3 It is it a kind that it is few as being chosen out of Si, germanium, Pb, and P, B and aluminum, and is Si, germanium, and P, B and aluminum preferably, and they are Si, and P, B and aluminum especially preferably. M5 It is it a kind that it is few as being chosen out of Li, Na, K, Rb, Cs, Mg, calcium, Sr, and Ba, is Cs and Mg preferably, and is Mg especially preferably. M7 It is it a kind that it is few as being chosen out of O and S, and is O preferably. p q It is 0.001-10 respectively, is 0.01-5 preferably, is 0.01-1.5 still more preferably, and is 0.7-1.5 especially preferably. r It is ** 1.00-50, is 1.00-26 preferably, and is 1.02-6 especially preferably.

[0021] Although the example of the negative-electrode material of this invention is shown below, this invention is not limited to these. SnAl 0.4B0.5P0.5K0.1O3.65 and SnAl0.4 B0.5 P0.5 Na 0.2O3.7, SnAl0.4 B0.3 P0.5 Rb 0.2O3.4, SnAl0.4 B0.5 P0.5 Cs0.1 O3.65, SnAl0.4 B0.5 P0.5 K0.1 germanium 0.05O3.85, SnAl0.4 B0.5 P0.5 K0.1 Mg0.1 germanium 0.02O3.83, and SnAl0.4 B0.4P0.4 O3.2, SnAl 0.3B0.5P0.2O2.7 and SnAl 0.3B0.5P0.2O2.7, SnAl0.4 B0.5 P0.3 Ba0.08Mg 0.08O3.26, SnAl0.4B0.4P0.4 Ba 0.08O3.28, SnAl 0.4B0.5P0.5O3.6, and SnAl0.4 B0.5 P0.5 Mg 0.1O3.7.

[0022] SnAl0.5 B0.4 P0.5 Mg0.1 F0.2 O3.65 and SnB0.5 P0.5 Li0.1 Mg 0.1F0.2O3.05, SnB0.5 P0.5 K0.1 Mg 0.1F0.2O3.05, SnB0.5 P0.5 K0.05Mg0.05F0.1 O3.03, and SnB0.5 P0.5 K0.05Mg 0.1F0.2O3.03, SnAl0.4 B0.5 P0.5 Cs0.1 Mg 0.1F0.2O3.65, SnB0.5 P0.5 Cs0.05Mg0.05F0.1 O3.03, and SnB0.5 P0.5 Mg0.1 F0.1 O3.05 and SnB0.5 P0.5 Mg0.1 F0.2 O3 and SnB0.5 P0.5 Mg0.1 F0.06O3.07 and SnB0.5 P0.5 Mg 0.1F0.14O3.03, SnPBa 0.08O3.58, SnPK 0.1O3.55, SnPK0.05Mg 0.05O3.58, SnPCs 0.1O3.55, SnPBa0.08F0.08O3.54, and SnPK0.1 Mg 0.1F0.2O3.55, SnPK0.05Mg0.05F0.1 O3.53, SnPCs0.1 Mg 0.1F0.2O3.55, SnPCs0.05Mg0.05F0.1 O3.53.

[0023] Sn1.1 aluminum 0.4B0.2P0.6 Ba0.08F0.08O3.54 and Sn1.1 aluminum0.4 B0.2P0.6 Li0.1 K0.1 Ba0.1 F0.1 O3.65 and Sn1.1 aluminum0.4 B0.4 P0.4 Ba 0.08O3.34, Sn1.1 aluminum0.4 PCs 0.05O4.23, Sn1.1 aluminum0.4 PK 0.05O4.23, and Sn1.2 aluminum0.5 B0.3 P0.4 Cs 0.2O3.5, Sn1.2 aluminum 0.4B0.2P0.6 Ba 0.08O3.68 and Sn1.2 aluminum0.4 B0.2 P0.6 Ba0.08F0.08O3.64, Sn1.2 aluminum0.4 B0.2P0.6 Mg0.04Ba 0.04O3.68, Sn1.2 aluminum0.4 B0.3 P0.5 Ba0.08O3.58, and Sn1.3 aluminum0.3 B0.3 P0.4 Na 0.2O3.3 and Sn1.3 aluminum0.2 B0.4 P0.4 calcium 0.2O3.4, Sn_{1.3} aluminum0.4 B0.4 P0.4 Ba 0.2O3.6, Sn1.4 aluminum0.4 PK 0.2O4.6, Sn1.4 aluminum0.2 Ba0.1 PK 0.2O4.45, and Sn1.4 aluminum0.2 Ba0.2 PK 0.2O4.6, Sn1.4 aluminum0.4 Ba0.2 PK0.2 Ba 0.1F0.2O4.9, Sn1.4 aluminum0.4 PK 0.3O4.65 and Sn1.5 aluminum0.2 PK 0.2O4.4, Sn1.5 aluminum0.4 PK 0.1O4.65, Sn1.5

aluminum0.4 PCs 0.05O4.63, Sn1.5 aluminum0.4 PCs0.05Mg 0.1F0.2O4.63.

[0024] SnSi0.5 aluminum0.1 B0.2 P0.1 calcium 0.4O3.1, SnSi0.4 aluminum 0.2B0.4O2.7 and SnSi0.5 aluminum0.2 B0.1 P0.1 Mg 0.1O2.8, SnSi0.6 aluminum 0.2B0.2O2.8, SnSi0.5 aluminum 0.3B0.4P0.2 O3.55 and SnSi0.5 aluminum0.3 B0.4 P0.5O4.30 and SnSi0.6 aluminum 0.1B0.1P0.3O3.25 and SnSi0.6 aluminum0.1 B0.1 P0.1 Ba 0.2O2.95, SnSi0.6 aluminum0.1 B0.1 P0.1 calcium0.2 O2.95, and SnSi0.6 aluminum0.4 B0.2 Mg 0.1O3.2, SnSi0.6 aluminum 0.1B0.3P0.1O3.05, and SnSi0.6 aluminum0.2 Mg 0.2O2.7, SnSi0.6 aluminum0.2 calcium 0.2O2.7 and SnSi0.6 aluminum 0.2P0.2O3, SnSi 0.6B0.2P0.2O3 and SnSi0.8 aluminum 0.2O2.9, SnSi0.8 aluminum 0.3B0.2P0.2O3.85 and SnSi 0.8B0.2O2.9, SnSi0.8 Ba 0.2O2.8, SnSi0.8 Mg 0.2O2.8, SnSi0.8 calcium 0.2O2.8, and SnSi 0.8P0.2O3.1.

[0025] Sn0.9 Mn 0.3B0.4P0.4 calcium0.1 Rb0.1 O2.95 and Sn0.9 Fe0.3 B0.4 P0.4 calcium0.1 Rb 0.1O2.95 and Sn0.8 Pb0.2 calcium0.1 P0.9 O3.35 and Sn0.3 germanium0.7 Ba0.1 P0.9 O3.35 and Sn0.9 Mn0.1 Mg 0.1P0.9O3.35, Sn0.2 Mn0.8 Mg 0.1P0.9O3.35, Sn0.7 Pb0.3 calcium 0.1P0.9O3.35, Sn0.2 germanium0.8 Ba 0.1P0.9O3.35.

[0026] The chemical formula of the compound which baking was carried out [above-mentioned] and obtained is computable from the weight difference of the fine particles before and behind baking as inductively-coupled-plasma (ICP) emission spectrochemical analysis and a shortcut method as a measuring method.

[0027] Although it is good until it approximates it to the deposition potential of the light metal, although 50-700-mol% per negative-electrode material of the amount of light metal insertion to the negative-electrode material of this invention is desirable, it is especially desirable, for example. [100-600 mol% of] Many the burst sizes are so desirable that there are to the amount of insertion. The insertion method of a light metal has electrochemical and the desirable chemical and thermal method. The method of inserting electrochemically the light metal contained in a positive active material and the method of electrochemical process of inserting directly electrochemically from a light metal or its alloy are desirable. The chemical method has mixture with a light metal, contact or an organic metal, for example, a butyl lithium etc., and the method of making it react. Electrochemical process and the chemical method are desirable. Especially this light metal has a lithium or a desirable lithium ion.

[0028] In this invention, by using the compound shown by the general formula (4) as shown above, and (5) mainly as a negative-electrode material, and the charge-and-discharge cycle property was more excellent, safety is high at high discharge voltage and high capacity, and the nonaqueous electrolyte rechargeable battery excellent in the high current characteristic can be obtained. the especially excellent effect is acquired in this invention -- things are made -- a thing is using the compound with which Sn's is contained and the valence of Sn exists with divalent as a negative-electrode material It can ask for the valence of Sn by chemical titration operation. For example, it can analyze by the method of a publication to 165 pages of Physics and Chemistry of Glasses Vol.8 No.4 (1967). Moreover, it is also possible to determine from the Knight shift by solid-state nuclear-magnetic-resonance (NMR) measurement of Sn. For example, it sets to broad measurement and Metal Sn (Sn of 0 **) is Sn (CH₃)₄. To receiving and a peak appearing in a low magnetic field extremely with near 7000 ppm, in SnO (= divalent), it appears near 100 ppm, and appears near -600 ppm in SnO₂ (= tetravalence). Thus, since a Knight shift is greatly dependent on the valence of Sn which is a central metal when it has the same ligand, the determination of a valence is attained in the peak position required in ¹¹⁹Sn-NMR measurement. Various compounds can be included in the negative-electrode material of this invention. For example, transition metals (Sc, Ti, V, Cr, Mn, Fe, Co, nickel, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, a lanthanoids system metal, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg) and a periodic-table 17 group element (F, Cl) can be included. Moreover, the dopant of the various compounds (for example, compound of Sb, In, and Nb) which raise electronic-conduction nature may also be included. 0-20-mol% of the amount of the compound to add is desirable.

[0029] the synthesis method of the multiple oxide which makes a subject the oxide shown by the general formula (4) in this invention, and (5) -- the calcinating method and a solution method -- any method is employable For example, it is M1 when the calcinating method is explained in detail. A compound and M2 A compound and M4 What is necessary is to mix a compound (for Si, germanium, Sn, Pb, P, B, aluminum, Sb, and M4 to be Mg, calcium, Sr, and Ba in difference for M1 and M2), and just to make it calcinate. As an Sn compound, for example, SnO, SnO₂, and Sn₂O₃, Sn₇O₁₃ and [Sn 3O₄ and] H₂O, Sn 8O₁₅, the first tin of hydroxylation, The second tin of oxy-hydroxylation, a stannous acid, a tin, the first tin of phosphoric acid, an ortho stannic acid, a metastannic acid, the Para stannic acid, a tin, the second tin of fluoridation, stannous chloride, a stannic chloride, the first tin of a pyrophosphoric acid, Lynn-ized tin, the first tin of sulfuration, a tin bisulfide, etc. can be mentioned. As an Si compound, hydro silane compounds, such as alkoxy silane compounds, such as organosilicon compounds, such as SiO₂, SiO, a tetramethylsilane, and a tetraethyl silane, a tetramethoxy silane, and a tetrapod ethoxy silane, and a TORIKURORO hydro silane, can be mentioned. As a germanium compound, alkoxy germanium compounds, such as GeO₂, GeO, a germanium tetrapod methoxide, and germanium tetrapod ethoxide, etc. can be mentioned. As a Pb compound, PbO₂, PbO, Pb₂O₃, Pb₃O₄, a lead nitrate, a

lead carbonate, a lead formate, lead acetate, a lead tetraacetate, tartaric-acid lead, lead JIETOKISHIDO, lead JI (isopropoxide), etc. can be mentioned. As a P compound, a phosphorus pentaoxide, phosphorus oxychloride, a phosphorus pentachloride, a phosphorus trichloride, phosphorus tribromide, a trimethyl phosphoric acid, a triethyl phosphoric acid, a TORIPURO pill phosphoric acid, the first tin of a pyrophosphoric acid, phosphoric-acid boron, etc. can be mentioned. As a B compound, for example, 32 boron oxide, boron trichloride, boron tribromide, a boron carbide, a way acid, way acid TORIMECHIRU, way acid triethyl, tripropyl borate, way acid tributyl, Lynn-ized boron, phosphoric-acid boron, etc. can be mentioned. As an aluminum compound, an aluminum oxide (an alpha alumina, beta alumina), an aluminum silicate, aluminum tree iso-propoxide, tellurous-acid aluminum, an aluminum chloride, HOU-ized aluminum, Lynn-ized aluminum, an aluminium phosphate, lactic-acid aluminum, way acid aluminum, an aluminum sulfate, an aluminum sulfate, HOU-ized aluminum, etc. can be mentioned. As a Sb compound, for example, 3 oxidation 2 antimony, triphenyl antimony, etc. can be mentioned.

[0030] As Mg, calcium, Sr, and a Ba compound, each oxidation salt, a hydroxylation salt, a carbonate, phosphate, a sulfate, a nitrate, an aluminium compound, etc. can be mentioned.

[0031] As baking conditions, it is 6 degrees C or more 2000 degrees C or less that it is 2000 degrees C or less of 4-degree-C [or more]/m programming rates as a programming rate desirable still more preferably. Are 10 degrees C or more 2000 degrees C or less, and it is especially preferably desirable as a burning temperature that it is [250 degrees-C or more] 1500 degrees C or less. It is 350 degrees C or more 1500 degrees C or less still more preferably, and is 500 degrees C or more 1500 degrees C or less especially preferably. And it is desirable that it is 100 or less hours as a firing time for 0.01 hours or more. It is 70 or less hours still more preferably for 0.5 hours or more, and is 20 or less hours especially preferably for 1 hour or more. And it is below 4-degree-C or more 107 ** that it is below 2-degree-C[or more]/m 107 ** as a temperature fall speed desirable still more preferably, and it is below 6-degree-C or more 107 ** especially preferably, and is 10 degrees C or more 107 degrees C or less especially preferably. The programming rate in this invention is the mean velocity of a temperature rise until it reaches "80% of burning temperature (degree-C display)" from "50% of burning temperature (degree-C display)", and the temperature fall speed in this invention is the mean velocity of a temperature reduction until it reaches "50% of burning temperature (degree-C display)" from "80% of burning temperature (degree-C display)." You may cool in a firing furnace and a temperature fall is taken out out of a firing furnace again, for example, may be supplied underwater and may be cooled. moreover, the gun method, the Hammer-Anvil method, and the slap method given in 217 pages (Gihodo Shuppan Co., Ltd. 1987) of ceramic processing -- the - gas atomizing method, the plasma-spraying method, a centrifugal quenching method, and melt Super-quenching methods, such as the drag method, can also be used. Moreover, you may cool using the single roller method given in 172 pages (Maruzen 1991) of new glass handbooks, and a congruence roller. In the case of the material fused during baking, you may take out a baking object continuously, supplying a raw material during baking. It is desirable to stir a melt in the case of the material fused during baking.

[0032] Oxygen content is the atmosphere below 5 volume % preferably, and baking gas atmosphere is inert gas atmosphere still more preferably. Nitrogen, an argon, helium, a krypton, a xenon, etc. are mentioned as inert gas.

[0033] The average grain size of the compound shown by the general formula (4) used by this invention and (5) has desirable 0.1-60 micrometers, especially its 1.0-30 micrometers are desirable, and its 2.0-20 micrometers are still more desirable. In order to make it a predetermined grain size, the grinder and classifier which were known well are used. For example, a mortar, a ball mill, a sand mill, a vibration ball mill, a satellite ball mill, a planet ball mill, a revolution air current type jet mill, a screen, etc. are used. At the time of trituration, wet grinding which made organic solvents, such as water or a methanol, live together can also be performed if needed. It is desirable to perform a classification in order to consider as a desired particle size. As the classification method, there is especially no limitation and it can use a screen, a pneumatic elutriation machine, an elutriation, etc. if needed. A classification can use dry type and wet.

[0034] It is more desirable to mix and compound so that the mole ratio of the sum total of a lithium compound / transition-metals compound (at least one sort chosen from Ti, V, Cr, Mn, Fe, Co, nickel, Mo, and W with transition metals here) may be set to 0.3-2.2 as a desirable lithium content transition-metals oxide positive-electrode material rather than being used by this invention. As an especially desirable lithium content transition-metals oxide positive-electrode material with which it is used by this invention, it is desirable to mix and compound so that the mole ratio of the sum total of a lithium compound / transition-metals compound (at least one sort chosen from V, Cr, Mn, Fe, Co, and nickel with transition metals here) may be set to 0.3-2.2. It is desirable that the especially desirable lithium content transition-metals oxide positive-electrode material used by this invention is Lix QOy (Q is mainly the transition metals in which a kind contains Co, Mn, nickel, V, and Fe at least here), x=0.02-1.2, and y=1.4-3. As Q, you may mix aluminum, Ga, In, germanium, Sn, Pb, Sb, Bi, Si, P, B, etc. in addition to transition metals. 0-30-mol% of the amount of mixtures is desirable to transition metals.

[0035] As a still more desirable lithium content metallic-oxide positive-electrode material used by this invention LixCoO_2 , LixNiO_2 , LixMnO_2 , and LixCoa nickel1-a O_2 , LixCob V1-b O_2 and LixCob Fe1-b O_2 , LixMn 2 O_4 , LixMnc Co2-c O_4 , and LixMnc nickel2-c O_4 , LixMnc V2-c O_4 and LixMnc Fe2-c O_4 (it is $x=0.02-1.2$, $a=0.1$ to 0.9 , $b=0.8$ to 0.98 , $c=1.6-1.96$, and $z=2.01-2.3$ here) are raised. As most desirable lithium content transition-metals oxide positive-electrode material used by this invention, LixCoO_2 , LixNiO_2 , LixMnO_2 , LixCoa nickel1-a O_2 , LixMn 2 O_4 , and LixCob V1-b O_2 (it is $x=0.02-1.2$, $a=0.1$ to 0.9 , $b=0.9$ to 0.98 , and $z=2.01-2.3$ here) are raised. Here, the x above-mentioned values are values before a charge-and-discharge start, and are fluctuated by charge and discharge.

[0036] If it is the electronic-conduction nature material which does not cause a chemical change in the constituted cell as a conductive carbon compound which can be used by this invention, it is good anything. As an example, carbon black, such as graphite, such as artificial graphites, such as elevated-temperature baking objects, such as natural graphites, such as a flaky graphite, a scale-like graphite, and an earthy graphite, petroleum coke, coal corks, celluloses, a saccharide, and a mesophase pitch, and a vapor-growth graphite, acetylene black, furnace black, KETCHIEN black, channel black, lamp black, and thermal black, an asphalt pitch, a coal tar, activated carbon, a meso fuze pitch, the poly acene, etc. can be raised. In these, graphite and carbon black are desirable. As electric conduction agents other than a carbon system, independent or such mixture can be included for conductive metallic oxides, such as conductive whiskers, such as metal powders, such as conductive fiber, such as a metal fiber, copper, nickel, aluminum, and silver, a zinc oxide, and a potassium titanate, and titanium oxide, etc. if needed.

[0037] the mixture of an electric conduction agent -- as for the addition to a layer, it is desirable that it is 6 - 50 % of the weight to negative-electrode material or positive-electrode material, and it is especially desirable that it is 6 - 30 % of the weight in carbon or a graphite, it is 6 - 20 % of the weight -- especially, it is desirable

[0038] the electrode used by this invention -- as a binder for holding a mixture, kinds or such mixture can be used for the polymer which has polysaccharide, thermoplastics, and rubber elasticity As a desirable binder, starch, a carboxymethyl cellulose, A cellulose, a diacetyl cellulose, a methyl cellulose, a hydroxyethyl cellulose, Hydroxypropylcellulose, alginic-acid Na, a polyacrylic acid, Polyacrylic-acid Na, a polyvinyl phenol, a polyvinyl methyl ether, Polyvinyl alcohol, a polyvinyl pyrrolidone, a polyacrylamide, Water-soluble polymer, such as PORIHIDOROKISHI (meta) acrylate and a styrene maleic-acid copolymer, Polyvinyl chloride, poly tetrapod FURURORO ethylene, a polyvinylidene fluoride, A tetrapod FURORO ethylene-hexa FURORO propylene copolymer, a vinylidene fluoride-tetrapod FURORO ethylene-hexa FURORO propylene copolymer, Polyethylene, polypropylene, an ethylene-propylene-diene terpolymer (EPDM), Sulfonation EPDM, a polyvinyl-acetal resin, a methylmetaacrylate, The acrylic-ester (meta) copolymer containing acrylic esters (meta), such as 2-ethylhexyl acrylate The polyvinyl ester copolymer containing vinyl esters, such as an acrylic-ester-acrylonitrile copolymer and vinyl acetate, (Meta) A styrene butadiene copolymer, an acrylonitrile butadiene copolymer, A polybutadiene, neoprene rubber, a fluororubber, a polyethylene oxide, An emulsion (latex) or suspensions, such as a polyester polyurethane resin, a polyether polyurethane resin, a polycarbonate polyurethane resin, polyester resin, phenol resin, and an epoxy resin, can be mentioned. The latex of a polyacrylic ester system, a carboxymethyl cellulose, a polytetrafluoroethylene, and a polyvinylidene fluoride are especially desirable. these binders are independent -- or it can mix and use if there are few additions of the binder -- an electrode -- if the holding power and cohesive force of a mixture are weak, and cycle nature is bad and there is again, electrode volume will increase, an electrode unit volume or the capacity per unit weight will decrease, conductivity falls further and capacity decreases [too many] Although especially the addition of a binder is not limited, its 1 - 30 % of the weight is especially desirable, and its 2 - 10 % of the weight is desirable.

[0039] the negative electrode of this invention -- a mixture or a positive electrode -- a mixture -- it is desirable to perform adjustment of a paste by the drainage system a mixture -- an active material and an electric conduction agent are mixed first, a binder (the suspension of resin fine particles or emulsion (latex)-like thing) and water are added, kneading mixture is carried out, succeedingly, it can distribute by stirring mixers, such as a mixer, a homogenizer, a dissolver, a planetary mixer, a paint shaker, and a sand mill, and the disperser, and adjustment of a paste can be performed the adjusted mixture of a positive active material or a negative-electrode active material -- on a charge collector, a paste is applied, (coat) dried and compressed and is mainly used Although an application can be performed by various methods, the reverse rolling method, the direct rolling method, the blade method, the knife method, the extrusion method, the curtain method, the gravure method, the bar method, the dipping method, and the squeeze method can be mentioned, for example. The blade method, the knife method, and the extrusion method are desirable. As for an application, it is desirable to carry out the speed for 0.1-100m/ under the present circumstances, a mixture -- according to the liquid nature of a paste, and a drying property, the surface state of a good application layer can be obtained by selecting the above-mentioned method of application Although the thickness, length, and width of the application layer are decided with the size of a cell, the thickness of an application layer is in the state compressed after

dryness, and especially its 1-2000 micrometers are desirable.

[0040] the method generally adopted can be used as a pellet, or the dryness for moisture removal of a sheet or the dehydration method, and independent in hot blast, a vacuum, infrared radiation, far infrared rays, an electron ray, and a damp wind -- or it can combine and use The range of temperature of 80-350 degrees C is desirable, and its range which is 100-250 degrees C is especially desirable. moisture content -- the cell whole -- 2000 ppm or less -- desirable -- a positive electrode -- a mixture and a negative electrode -- it is desirable to make it 500 ppm or less in a mixture or the electrolytic solution, respectively in respect of charge-and-discharge cycle nature

[0041] a sheet-like electrode -- although compression of a mixture can use the press method generally adopted, a die-press method and its calender pressing method are especially desirable Especially press ** is 10 kg/cm² - 3 t/cm², although not limited. It is desirable. The press speed of the calender pressing method has the amount of desirable 0.1-50m/. Press temperature has desirable room temperature -200 degree C.

[0042] As the quality of the material, in a positive electrode, it is aluminum, stainless steel, nickel, titanium, or these alloys, the base materials, i.e., the charge collector, of the positive electrode which can be used by this invention, and a negative electrode, they are copper, stainless steel, nickel, titanium, or these alloys at a negative electrode, and are a foil, an expanded metal, a punching metal, and a wire gauze as a gestalt. Especially, in a positive electrode, copper foil is desirable to an aluminum foil and a negative electrode.

[0043] The separator which can be used by this invention has large ion transmittance, and it has a predetermined mechanical strength, and that what is necessary is just an insulating thin film, as the quality of the material, olefin system polymer, fluorine system polymer, cellulose system polymer, a polyimide, nylon, a glass fiber, and an alumina fiber are used, and a nonwoven fabric, textile fabrics, and a microporosity film are used as a gestalt. Especially, as the quality of the material, the mixture of polypropylene, polyethylene, polypropylene, the mixture of polyethylene and polypropylene, and Teflon and the mixture of polyethylene and Teflon are desirable, and what is a microporosity film as a gestalt is desirable. Especially, the microporosity film whose thickness an aperture is 0.01-1 micrometer and is 5-50 micrometers is desirable.

[0044] The configuration of a cell is applicable to both a button, coin a sheet a cylinder an angle, etc. A cell inserts in a cell can the electrode wound with a pellet, the shape of a sheet, and the separator, connects an electrode with a can electrically, and the electrolytic solution is poured in, and it obturates and forms it. At this time, a relief valve can be used as an obturation board. Furthermore, in order to guarantee the safety of a cell, it is desirable to use a PTC element.

[0045] The closed-end cell sheathing cans which can be used by this invention are the steel board which performed nickel plating as the quality of the material, a stainless steel plate (SUS304, SUS304 L, SUS304 N, SUS316, SUS316 L, SUS430, SUS444 grade), the stainless steel plate (same as the above) which performed nickel plating, aluminum or its alloy, nickel, titanium, and copper, and are perfect circle form tubed one, ellipse form tubed one, square tubed, and rectangle tubed as a configuration. Especially when a sheathing can serves as a negative-electrode terminal, a stainless steel plate and the steel board which performed nickel plating are desirable, and when a sheathing can serves as a positive-electrode terminal, a stainless steel plate, aluminum, or its alloy is desirable.

[0046] the mixture of the shape of this sheet -- an electrode is rolled or folded, is inserted in a can, connects a sheet with a can electrically, pours in the electrolytic solution, and forms a cell can using an obturation board At this time, a relief valve can be used as an obturation board. It may be equipped with the various safe elements known from the former besides a relief valve. For example, a fuse, bimetal, a PTC element, etc. are used as an overcurrent-protection element. Moreover, the method, the gasket crack method, or the obturation board crack method of making a cut in a cell can can be used for everything but a relief valve as a cure of internal pressure elevation of a cell can. Moreover, you may make the circuit which built the surcharge and the cure against an overdischarge into the charge machine provide.

[0047] Although the electrolytic solution may pour in the whole quantity at once, it is desirable to carry out by dividing into two or more stages. When dividing and pouring into two or more stages, the composition (after pouring in the solution which dissolved lithium salt in the non-aqueous solvent or the non-aqueous solvent, the solution which dissolved lithium salt in a non-aqueous solvent or a non-aqueous solvent with viscosity higher than the aforementioned solvent is poured in) which is different also by the same composition is sufficient as each liquid. Moreover, a cell can may be decompressed for shortening of the pouring time of the electrolytic solution etc. (preferably 500 - 1 torr, more preferably 400 - 10 torr), or you may perform applying a centrifugal force and an ultrasonic wave to a cell can.

[0048] A metal and an alloy with electrical conductivity can be used for a can or a lead board. For example, metals or those alloys, such as iron, nickel, titanium, chromium, molybdenum, copper, and aluminum, are used. A well-known method (electric welding of an example, a direct current, or an alternating current, laser welding, ultrasonic welding)

can be used for the welding process of a cap, a can, a sheet, and a lead board. The compound and mixture which are known from the former, such as asphalt, can be used for the sealing compound for obturation.

[0049] As the quality of the material, they are olefin system polymer, fluorine system polymer, cellulose system polymer, a polyimide, and a polyamide, from organic-solvent-proof nature and low-water-flow part permeability, the gasket which can be used by this invention has desirable olefin system polymer, and especially its polymer of a propylene subject is desirable. Furthermore, it is desirable that it is the block copolymerization polymer of a propylene and ethylene.

[0050] The cell of this invention is covered with a sheathing material if needed. As a sheathing material, there are heat-shrinkable tubing, an adhesive tape, a metal film, paper, cloth, a paint, a plastics case, etc. Moreover, the portion of sheathing discolored with heat in part at least is prepared, and you may make it the heat history in use known. The cell of this invention constructs two or more in series and/or in parallel if needed, and is contained by the cell pack. You may prepare a safety circuit (circuit with the function which intercepts current if it acts as the monitor of the voltage of each cell and/or the whole group cell, temperature, the current, etc. and is required) besides safe elements, such as a right temperature coefficient resistor, a thermal fuse, a fuse, and/or a current interception element, in a cell pack. Moreover, the positive electrode of each cell and a negative-electrode terminal, the whole group cell and the temperature element child of each cell, the current element child of the whole group cell, etc. can also be prepared in a cell pack as an external terminal in addition to the positive electrode of the whole group cell, and a negative-electrode terminal. Moreover, you may build voltage conversion circuits (DC-DC converter etc.) in a cell pack. Moreover, it may fix by welding a lead board, and you may fix connection of each cell so that it can detach and attach easily with a socket etc. Furthermore, you may prepare display functions, such as cell remaining capacity, existence of charge, and a usage count, in a cell pack.

[0051] The cell of this invention is used for various devices. It is desirable to be especially used for a video movie, a carrying type videocassette recorder with a built-in monitor, a movie camera with a built-in monitor, a compact camera, a single-lens reflex camera, a disposable camera, a notebook sized personal computer, a note type word processor, an electronic notebook, a cellular phone, a cordless telephone, a mustached camber, a power tool, an electric mixer, an automobile, etc.

[0052]

[Example] Although an example is raised to below and this invention is explained in more detail, unless the main point of invention is exceeded, this invention is not limited to an example.

[0053] [positive electrode -- a mixture -- example [of a paste] of creation; -- example and example of comparison] -- positive-active-material; LiCoO₂ (what put into the alumina crucible what was mixed with a lithium carbonate and 4 oxidization 3 cobalt by the mole ratio of 3:2, calcinated at 900 degrees C for 8 hours, and was further cracked at them at the speed of 2 degrees C/m at the temperature of temperature up Perilla frutescens (L.) Britton var. crispa (Thunb.) Decne. after carrying out the temperature up to 750 degrees C and carrying out temporary quenching to them at 2 degrees C/m for 4 hours, among air In 200g and acetylene black 10g, a 0.6 mS/m specific surface area [electric conductivity / of the distributed liquid when distributing centriole child size 5micrometer and 50g of washing articles in 100ml water] / according / pH / to 10.1 and a nitrogen adsorption process is mixed with a homogenizer, continues 0.42m² / g, and is as a binder. 2-ethylhexyl acrylate, an acrylic acid, and the water distribution object (50 % of the weight of solid-content concentration) of the copolymer of acrylonitrile -- 8g and carboxymethyl-cellulose solution of 2 % of the weight of concentration -- 60g -- adding -- kneading mixture -- carrying out -- further -- water -- 50g -- adding -- a homogenizer -- stirring mixture -- carrying out -- a positive electrode -- a mixture -- the paste was created [negative electrode -- a mixture -- example of creation] of a paste -- negative-electrode active material; -- SnGe0.1 B0.5 P0.58Mg 0.1K0.1O3.35 (6.7g of tin protoxides) 10.3g of pyrophosphoric-acid tin, 1.7g of boron oxides, 0.7g of potassium carbonate, 0.4g [of magnesium oxides] and diacid-ized germanium 1.0g is blended dryly. Put into the crucible made from an alumina and a temperature up is carried out to 1000 degrees C by part for bottom 15-degree-C/of argon atmosphere. Collect what lowered even to the room temperature by part for 10-degree-C/, and was taken out from the firing furnace, and set to the X-ray diffraction method using what was ground with the jet mill, 4.5 micrometers of mean particle diameters, and CuK alpha rays, after calcinating at 1100 degrees C for 12 hours. It is the object which has the broadcloth peak which has the peak near 28 degree with 2theta value. the crystalline diffraction line was not looked at by 40 degrees or more 70 degrees or less with 2theta value It mixes with 30g and a homogenizer. 200g and an electric conduction agent (artificial graphite) -- the thing and water which furthermore added 50g of carboxymethyl-cellulose solution of 2 % of the weight of concentration, and 10g of polyvinylidene fluorides as a binder, and were mixed -- 30g -- adding -- further -- kneading mixture -- carrying out -- a negative electrode -- a mixture -- the paste was created

[creation of a positive electrode and a negative-electrode electrode sheet] -- the positive electrode created above -- a mixture -- after having applied the paste to both sides of an aluminum foil charge collector with a thickness of 30 micrometers by the blade coating machine so that the thickness of the sheet after coverage 400 g/m² and compression might be set to 280 micrometers, and drying it, compression molding was carried out with the roller-press machine, it judged in the predetermined size, and the band-like positive-electrode sheet was created Furthermore, dehydration dryness was enough carried out at the far-infrared heater in the dry box (dew-point; dry air of -50-degree-C or less **), and the positive-electrode sheet was created. the same -- a negative electrode -- a mixture -- the paste was applied to the 20-micrometer copper foil charge collector, and the negative-electrode sheet whose thickness of the sheet after coverage 70 g/m² and compression is 90 micrometers was created by the same method as the above-mentioned positive-electrode sheet creation

[Example of electrolytic-solution adjustment (examples 1-15)] In argon atmosphere, 65.3g diethyl carbonate was put into the polypropylene container of a 200 cc thin mouth, and the 22.2g ethylene carbonate was dissolved small quantity every, taking care that solution temperature does not exceed 30 degrees C to this. Next, 0.4g LiBF₄ and 12.1g LiPF₆ It dissolved in the above-mentioned polypropylene container small quantity every in order, respectively, taking care that solution temperature does not exceed 30 degrees C. The obtained electrolytic solution was a transparent and colorless liquid by specific gravity 1.135. The amount of [18 ppm (Kyoto electron make tradename MKC-210 type car RUFI shear water measurement equipment measurement) and] free acid of moisture was 24 ppm (the bromthymol blue is used as an indicator, a neutralization titration is carried out using decinormal NaOH solution, and it measures). Furthermore, the compound given in this electrolytic solution in Table 1 was dissolved, respectively so that it might become predetermined concentration, and the electrolytic solution was adjusted.

[Example of creation of a cylinder cell] The laminating was carried out to the order of a positive-electrode sheet, the separator made from a microporosity polypropylene film, a negative-electrode sheet, and a separator, and this was wound in the shape of a whorl. It contained with the iron closed-end cylindrical cell can which performed nickel plating which serves this winding object as a negative-electrode terminal. The electrolytic solution which furthermore added the additive of a publication to Table 1 as the electrolytic solution was poured in into the cell can. the cell lid which has a positive-electrode terminal -- a gasket -- minding -- the cylindrical cell was created in total

[0054] [Example 1 of comparison] By the same method as an example, the cylindrical cell was created using the electrolytic solution which is not adding the additive.

[Examples 2-3 of comparison] It changed into the oxide system negative-electrode active material, the negative-electrode sheet was created by the same method as creation of the aforementioned negative-electrode sheet using the carbon system active material (graphite powder), and the cylindrical cell was created, using the electrolytic solution of Table 1 respectively.

[0055] About the cell created by the above-mentioned method, charge and discharge were carried out on condition that current density 5 mA/cm², charge final-voltage 4.1V, and discharge-final-voltage 2.8V, and service capacity and the cycle life were searched for. The ratio and cycle nature (300th capacity to the 1st charge and discharge comparatively) of capacity (Wh) of each cell are shown in Table 1.

[0056]

Table 1 Experimental-result experimental run number Additive Addition concentration Initial capacity SAIRU nature (%)

(A mol/liter) (%) . Example 1 Trimethyl phosphate 0.001 1.0 80 Example 2 Trimethyl phosphate 0.01 0.98 81 Example 3 Trimethyl phosphate 0.05 0.97 82 Example 4 Trioctyl phosphate 0.001 1.0 85 Example 5 Trioctyl phosphate 0.01 1.01 85 examples 6 Trioctyl phosphate 0.051.0 87 Example 7 Triphenyl phosphate 0.01 0.99 84 Example 8 TORIBUTOKISHIECHIRUHOSU 0.010.9883 FETO example 9 Tricresyl phosphate 0.011.01 86 An example 10 Tris 0.01 (chloro ethyl) 0.99 84 Phosphate example 11 tributyl phosphate 0.01 1.02 88 Example 12 Methyl-ethylene HOSUFE 0.01 0.96 82 - TO example 13 Phenyl ECHIRENHOSU 0.01 0.98 86 FETO example 14 Trimethylolethane 0.01 1.0 82 Phosphate example 15 Methyl diethyl HOSUFE 0.01 1.0 82 Example 1 of - TO comparison Nothing 0 1.0 70 Example 2 of comparison Nothing 0 0.80 75 Example 3 of comparison Trimethyl phosphate 0.01 0.8180. [0057] To the cell which used the carbon system negative-electrode active material, the cell which used the oxide system negative-electrode active material of this invention has a large capacity, and cycle nature's by trialkyl phosphate addition is improving further, and the rate of improvement is larger than what used the carbon system negative-electrode active material.

[0058]

[Effect of the Invention] By the electrolytic solution which contained trialkyl phosphate like this invention, it has the outstanding charge-and-discharge property, and a nonaqueous electrolyte rechargeable battery with still less

degradation of the service capacity by the charge-and-discharge repeat can be obtained.

[Translation done.]